Supporting Information

Reduction of Uranyl in the Interlayer Region of Low Iron Micas Under Anoxic and Aerobic Conditions

Eugene S. Ilton*[1], Steve M. Heald[1], Steven C. Smith[1], David Elbert[2] and Chongxuan1 Liu[1]

[1]Pacific Northwest National Laboratory, 902 Battelle Boulevard, MS: K8-96, Richland, WA 99352; [2]Johns Hopkins Univerisity, Dept. of Earth & Planetary Sciences, Baltimore MD, 21218.

*Corresponding Author:
Eugene.Ilton@pnl.gov
509 376 5022

Model description:

Assuming that Fe(II) supply was sufficiently large relative to the low concentration

of U(VI), diffusion and reduction of U(VI) can be described by two models

depending on whether U^R, the reduced species (V$\pm$IV), is diffusible or not. When U^R

is not diffusible, the reactive diffusion of U(VI) and U^R can be mathematically

described as follows:

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial x^2} - kc_1 \tag{1}$$

$$\frac{\partial c_2}{\partial t} = kc_1 \tag{2}$$

where c_1 and c_2 are the concentrations of U(VI) and U^R, respectively, D is the

apparent diffusivity, k is the first-order rate constant of U(VI) reduction to U^R, x is

the distance from the solid/solution interface (boundary), and t is the time. The

boundary concentration of U(VI) at solid/solution interface was assumed to be equal

to U(VI) concentration in solution (i.e., c_0), and initial U(VI) in the mica was

assumed to be zero. With these boundary and initial conditions, Eq 1 has an

analytical solution:

$$\frac{c_1}{c_0} = \frac{1}{2}\left(\exp(-\sqrt{\frac{k}{D}}x)(1 - erf(\frac{x}{2\sqrt{Dt}} - \sqrt{kt})) + \exp(\sqrt{\frac{k}{D}}x)(1 - erf(\frac{x}{2\sqrt{Dt}} + \sqrt{kt}))\right) \tag{3}$$

where $erf(x)$ is the error function. Eq 2 has a form:

$$c_2 = k\int_0^t c_1(x,\tau)d\tau \tag{4}$$

Eq 4 was numerically evaluated by Gaussian Quadratures.

To determine parameters k and D in Eq 3, the model was used to fit the total

measured intensity as a function of distance (Figure 1 in paper). In the fitting, we first

calculated the U(VI) diffusion profile from Eq 3, and total U after addition of U^R from Eq

4 with trial parameter k and D. These profiles were shown as "single" profiles in Figure 5

(in the paper) and were assumed to be profiles within individual mica interlayers.

Because the mica edge was not a mathematical plane as shown by the adsorption profile

(Figure 1, in the paper), these diffusion profiles were shifted spatially to reflect the

changes of solid/solution boundaries for different mica interlayers. These shifted

diffusion profiles were then combined for each spatial distance x. To match the

procedures of experimental data processing, the combined diffusion profiles were then

normalized to the highest concentration in the total U concentration profile. The

parameter k and D were then adjusted, and normalized profiles were re-calculated again

until the calculated best fit with the measurements. The best fit yielded $D = 3 \times 10^{-15}$ m^2/s,

and $k = 2.1 \times 10^{-5}$ s^{-1}. The calculated ratio of U(VI)/U$_{tot}$ ranged from 0.36 to 0.42 from

-520 to -550 μm with an average of 0.39.

When U^R is diffusible, the reactive diffusion of U(VI) and U^R can be

mathematically described by following equations:

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial x^2} - kc_1 \qquad (5)$$

$$\frac{\partial c_2}{\partial t} = KD \frac{\partial^2 c_2}{\partial x^2} - kc_1 \qquad (6)$$

Variable K is the ratio of U^R and U(VI) diffusivity and other symbols are defined as

before. A zero U^R boundary concentration was assumed at the interface between the

mica and bulk solution and a no mass flux condition is imposed at the interior of the

mica. Boundary conditions for U(VI) and initial conditions for U(VI) and U^R are assumed to be the same as described before. With these boundary and initial conditions, Eq 5 has the same analytical solution as Eq 3:

$$\frac{c_1}{c_0} = \frac{1}{2}\left(\exp(-\sqrt{\frac{k}{D}}x)(1 - erf(\frac{x}{2\sqrt{Dt}} - \sqrt{kt})) + \exp(\sqrt{\frac{k}{D}}x)(1 - erf(\frac{x}{2\sqrt{Dt}} + \sqrt{kt})) \right) \quad (6)$$

Eq 6 has a form:

$$c_2 = \frac{k}{2\sqrt{KD\pi}} \int_0^t \frac{d\tau}{\sqrt{t - \tau}} \int_0^{+\infty} c_1(\xi, t) \left(\exp\left(-\frac{(x - \xi)^2}{4KD(t - \tau)} \right) - \exp\left(-\frac{(x + \xi)^2}{4KD(t - \tau)} \right) \right) d\xi \quad (7)$$

Eq 7 was numerically evaluated by Gaussian Quadratures.

Parameters k and D in Eqs 6 and 7 were determined by fitting the experimental values of total U, as described before. Parameter K was used in sensitivity tests. The fitted k and D are close to those determined when U^R was assumed non diffusible. Sensitivity tests showed that K has to be less than 0.001 in order to fit the experimental results, suggesting that U^R diffused at a much slower rate than U(VI).